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STRUCTURE AND PROPERTIES OF NOVEL COMPOUNDS OF SILICON
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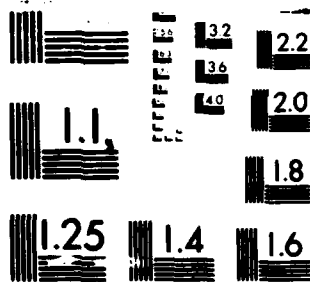
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Dr. Josef Michl

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Work on silanimines has been continued in collaboration with Professor R. West (Madison, Wisconsin). A highly sterically hindered derivative has been found to be stable in solutions at low temperature. The controversy concerning the assignment of the structure of dimethylsilylene by Drahnak, West, and Michl has now been settled. The pyrolysis of phenyltriazidosilane yields phenylsilaisonitrile and this has been confirmed by chemical trapping as well as UV and IR matrix-isolation spectroscopy. We have discovered that the photolysis of $\text{PhSi}(\text{N}_3)_3$ in matrix isolation produces not only PhNSi , but also the isomer, benzosilanitrile. This is the first representative of a triply bonded compound of tetravalent silicon.

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**FINAL
TECHNICAL REPORT**

**Structure and Properties of Novel Compounds of
Silicon Germanium and Tin**

Josef Michl, Principal Investigator
Department of Chemistry
University of Utah
Salt Lake City, UT 84112

June 1, 1985 - August 1, 1986

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COMPLETED PROJECT SUMMARY

1. Title: STRUCTURE AND PROPERTIES OF NOVEL COMPOUNDS OF SILICON GERMANIUM AND TIN
2. Principal Investigator: Dr. Josef Michl
Department of Chemistry, University of Utah,
Salt Lake City, UT 84112
3. Inclusive Dates: February 1, 1984 - September 30, 1985
4. Grant Number: AFOSR-84-0065 Amend A
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6. Senior Research Personnel: Dr. Laszlo Fabry, Dr. Dieter Littmann, Dr. Karl Reuter, Dr. John Downing, Dr. Gerhard Gross, and Dr. Gerhard Raabe
7. Junior Research Personnel: Mr. Jeffrey Fisher, Mr. Kevin Welsh, Mr. Steven Zigler
8. Publications: Please see attached list
9. Abstract of Objectives and Accomplishments:

The objective of our work has been to enhance the knowledge of the molecular structure, electronic structure, and reactivity of a series of novel compounds characterized by the presence of divalent or multiply bonded silicon or its heavier analogs, starting from a new type of photochemical precursor and using low-temperature matrix isolation spectroscopy and quantum mechanical calculations.

Because of the move of my research group to the University of Texas, this final report covers only two years of work. In this period, we have: (i) synthesized a series of geminal polyazides and demonstrated their utility in the production of matrix-isolated silylenes and germylenes from diazides and of silicon analogs of a nitrile and an isonitrile from a triazide, (ii) completed a definitive characterization of dimethylsilylene, leading to a satisfactory resolution of the extended literature controversy (Dr. Griller has now retracted in print his objections to our original assignment), (iii) completed a definitive IR characterization of 1-methylsilylene, (iv) characterized a large series of silylenes and disilenes by UV spectra and trapping reactions, (v) obtained complete structural characterization of the adducts of oxygen to disilenes, (vi) obtained the first directly observed free silanimine, (vii) characterized the π -acceptor and π -donor strengths of a series of polysilane substituents, (viii) written a comprehensive review on the chemistry of multiply bonded silicon. Most of the work was done in collaboration with Prof. R. West from the University of Wisconsin at Madison.

AFOSR Program Manager: Dr. Matuszko

CUMULATIVE LIST OF PUBLICATIONS WHICH ACKNOWLEDGE SUPPORT OF AFOSR 84-0065

1. H. Vancik, G. Raabe, M. J. Michalczyk, R. West and J. Michl, "Dimethylsilylene: A Trisilane and a Geminal Diazide as New Photochemical Precursors. Evidence for an Absorption Maximum near 450 nm", J. Am. Chem. Soc. 107, 4097 (1985).
2. M. J. Michalczyk, M. J. Fink, D. J. DeYoung, C. W. Carlson, K. M. Welsh, R. West, and J. Michl, "Organosilylenes and Their Dimerization to Disilenes", Silicon, Germ., Tin and Lead Comp., 2, 75 (1986).
3. M. J. Michalczyk, M. J. Fink, K. J. Haller, R. West, and J. Michl, "Structural and Chemical Properties of 1,3-cyclodisiloxanes", Organometallics 5, 531 (1986).
4. G. Raabe, H. Vancik, R. West, and J. Michl, "IR Transition Moment Directions in Matrix-Isolated Dimethylsilylene and 1-Methylsilylene", J. Am. Chem. Soc. 108, 671 (1986).
5. D. L. Bean, K. M. Welsh, R. West, and J. Michl, "Photochemistry of a Matrix-Isolated Geminal Diazide: Dimethylgermylene and Tetramethyldigermene", submitted for publication.
6. G. Raabe and J. Michl, "Multiple Bonding to Silicon", Chem. Reviews 85, 419 (1985).
7. G. H. Weeks, W. Adcock, K. A. Klingensmith, J. W. Waluk, R. West, M. Vasak, J. Downing, and J. Michl, "A Probe for Substituent Hyperconjugative Power: Magnetic Circular Dichroism of the Benzene L_b Band", Pure and Appl. Chem. 58, 39 (1986).
8. S. Zigler, R. West, and J. Michl, "Observation of a Stable Silanimine in an Inert Matrix and in Solution at Low Temperature", Chem. Lett., 1025 (1986).
9. A. Sekiguchi, S. S. Zigler, R. West, and J. Michl, "A Synthon for the Silicon-Silicon Triple Bond", J. Am. Chem. Soc. 108, 4241 (1986).

FINAL TECHNICAL REPORT OF ACTIVITIES AT THE UNIVERSITY OF UTAH

(June 1, 1985 - August 1, 1986)

1. Work on silanimines ($\text{Si}=\text{N}$ compounds) has been continued in collaboration with Prof. R. West (Madison, Wisconsin). A highly sterically hindered derivative has been found to be stable in solutions at low temperature. The results have been published. A mixture of two isomeric di-*t*-butylsilanimines (Si_2Si - and Si_2N -substituted) have now been characterized both by chemical trapping and matrix-isolation spectroscopy. A separation of their spectra is very difficult and has not been accomplished yet.

2. Also in collaboration with Prof. R. West, irradiation of matrix-isolated di-*t*-butyldiazidosilane has been found to yield four products. One of these has been characterized completely by trapping as well as spectroscopy and is di-*t*-butylsilylene. It is a ground-state singlet. It can be photorearranged into a product which we are now trying to identify.

The characterization of the second product from $\text{t-Bu}_2\text{Si}(\text{N}_3)_2$ is also almost complete: it is the first $-\text{N}=\text{Si}=\text{N}-$ compound, *N,N*-di-*t*-butylsilanediiimine.

The third and fourth photoproducts are found in minor amounts and have not yet been identified.

3. The controversy concerning the assignment of the structure of dimethylsilylene, Me_2Si : by Drahnak, West, and Michl has now been settled. Dr. Griller, who questioned the assignment in print as incompatible with his flash photolytic evidence, has reported at the New York City ACS meeting in April, 1986, and as an Erratum in JACS, that his results were distorted by impurities and that he no longer questions our assignment.

4. The pyrolysis of phenyltriazidosilane, $\text{PhSi}(\text{N}_3)_3$, yields phenylsilaisonitrile, PhNSi :, and we have confirmed this by chemical trapping as well

as UV and IR matrix-isolation spectroscopy. The first published report of this result is, however, due to Prof. H. Bock (Frankfurt, West Germany), who characterized the pyrolysis product by photoelectron spectroscopy, beating us to the goal.

However, we are likely to recover well from this loss: we have discovered more recently that the photolysis of $\text{PhSi}(\text{N}_3)_3$ in matrix isolation produces not only PhNSi , as we knew a year ago, but also the isomer, benzosilanitrile $\text{PhSi}\equiv\text{N}$. This is the first representative of a triply bonded compound of tetravalent silicon. We have characterized this species by chemical trapping and IR and UV spectroscopy and have reported the results at the XXth Organosilicon Symposium in Tarrytown, New York in April, 1986. The results have not been submitted for publication as yet, since isotopic substitution studies needed for the full IR analysis have not been completed.

5. The magnetic circular dichroism of a series of benzenes carrying Si, Ge, or Sn-based substituents has been recorded and information was obtained on the substituent π -donor and π -acceptor power. These results have been published. This was done in collaboration with Prof. R. West.

6. Progress has been made towards a $\text{Si}\equiv\text{Si}$ bond, for which a synthon has now been developed. The bulk of this work was, however, done in the laboratory of Prof. R. West at the University of Wisconsin in Madison. A short communication has been published.

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